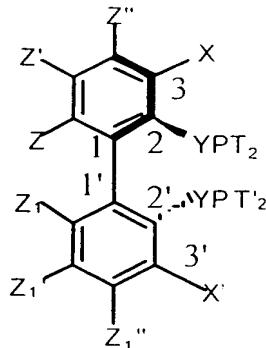


**WHAT IS CLAIMED IS:**

1. A ligand represented by the formula or its enantiomer:

5



wherein each X and X' is independently selected from the group  
10 consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR<sub>2</sub>, COOR, halide, SiR<sub>3</sub>, P(O)R<sub>2</sub>, P(O)(OR)<sub>2</sub> and P(OR)<sub>2</sub>;  
wherein each Z and Z<sub>1</sub> is independently selected from the group consisting  
of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR<sub>2</sub>, COOR, halide,  
SiR<sub>3</sub>, P(O)R<sub>2</sub>, P(O)(OR)<sub>2</sub> and P(OR)<sub>2</sub>; or wherein Z and Z<sub>1</sub> together form the  
15 bridging group A-B-A<sub>1</sub>;  
wherein each Z', Z'', Z<sub>1</sub>' and Z<sub>1</sub>'' is independently selected from the group  
consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR<sub>2</sub>,  
COOR, halide, SiR<sub>3</sub>, P(O)R<sub>2</sub>, P(O)(OR)<sub>2</sub> and P(OR)<sub>2</sub>; or wherein Z' and Z  
together form the bridging group A'-B-A; Z' and Z together form a fused  
20 cycloaliphatic or aromatic group; Z<sub>1</sub> and Z<sub>1</sub>' together form the bridging group A<sub>1</sub>-  
B<sub>1</sub>-A<sub>1</sub>'; and/or Z<sub>1</sub> and Z<sub>1</sub>' together form a fused cycloaliphatic or aromatic group;  
wherein each A, A', A<sub>1</sub> and A<sub>1</sub>' is independently selected from the group  
consisting of: O, CH<sub>2</sub>, NH, NR, S, CO and a bond;  
wherein each B and B<sub>1</sub> is independently selected from the group consisting  
25 of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12

carbon atoms, O, CH<sub>2</sub>, NH, NR, S, CO, SO<sub>2</sub>, P(O)R, P(O)OR, POR, SiR<sub>2</sub> and a bond;

wherein each T is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R'', YR', 5 YR'', Y'R' and Y''R'; or wherein two T groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each T' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R'', YR', 10 YR'', Y'R' and Y''R'; or wherein two T' groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each R, R' and R'' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, aralkyl and alkaryl of 1 to 22 carbon atoms; or wherein two R groups, two R' groups or two R'' group together form an alkylene, arelene or substituted arylene group; and 15

wherein each Y, Y' and Y'' is independently selected from the group consisting of: O, CH<sub>2</sub>, NH, S and a bond between carbon and phosphorus; with the proviso that when the Y group at the 2' position is a bond between carbon and phosphorus, X' is hydrogen.

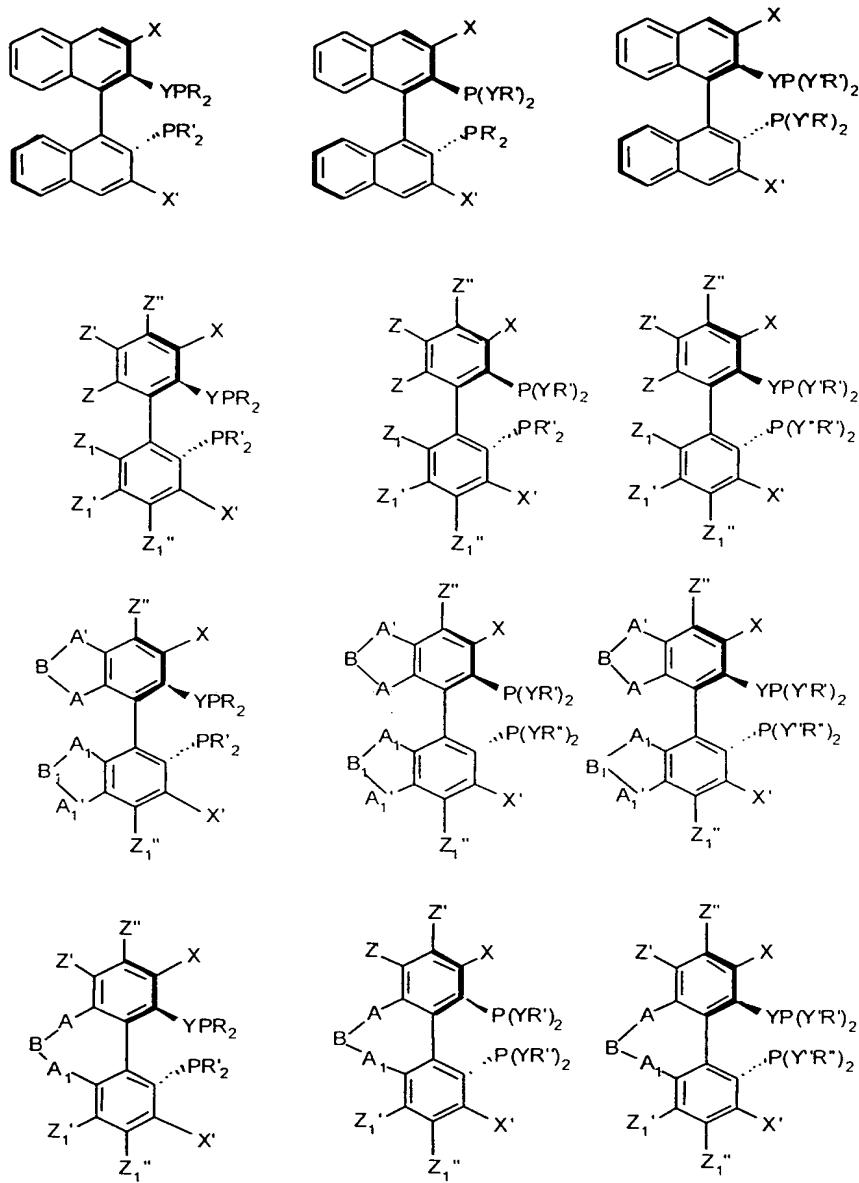
20 2. The ligand of claim 1, wherein said substituted alkyl has one or more substituents, each independently selected from the group consisting of: halogen, ester, ketone, carboxylic acid, hydroxy, alkoxy, aryloxy, thiol, alkylthio and dialkylamino.

25 3. The ligand of claim 1, wherein said alkylene is selected from the group consisting of compounds represented by the formula: -(CH<sub>2</sub>)<sub>n</sub>-, wherein n is an integer in the range of from 1 to 8.

30 4. The ligand of claim 1, wherein each of said aryl groups optionally has one or more substituents, each independently selected from the group consisting of: halogen, ester, ketone, sulfonate, phosphonate, hydroxy, alkoxy,

aryloxy, thiol, alkylthiol, nitro, amino, vinyl, substituted vinyl, carboxylic acid, sulfonic acid and phosphine.

5. The ligand of claim 1, wherein each of said arylene groups optionally has one or more substituents, each independently selected from the group consisting of: halogen, ester, ketone, sulfonate, phosphonate, hydroxy, alkoxy, aryloxy, thiol, alkylthiol, nitro, amino, vinyl, substituted vinyl, carboxylic acid, sulfonic acid and phosphine.
- 10 6. The ligand of claim 1, wherein each of said arylene groups is independently selected from the group consisting of: 1,2-divalent phenyl, 2,2'-divalent-1,1'-biphenyl, 2,2'-divalent-1,1'-binaphthyl and ferrocene.
- 15 7. The ligand of claim 1, wherein said ligand is a racemic mixture of enantiomers.
8. The ligand of claim 1, wherein said ligand is a non-racemic mixture of enantiomers.
- 20 9. The ligand of claim 1, wherein said ligand is one of the enantiomers.
10. The ligand of claim 1, having an optical purity of at least 85% ee.
- 25 12. The ligand of claim 1, having an optical purity of at least 95% ee.
13. The ligand of claim 1, wherein said ligand is selected from the group consisting of compounds represented by the following formulas:



wherein each X and X' is independently selected from the group  
 5 consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR<sub>2</sub>, COOR, halide, SiR<sub>3</sub>, P(O)R<sub>2</sub>, P(O)(OR)<sub>2</sub> and P(OR)<sub>2</sub>;  
 wherein each Z and Z<sub>1</sub> is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR<sub>2</sub>, COOR, halide,

SiR<sub>3</sub>, P(O)R<sub>2</sub>, P(O)(OR)<sub>2</sub> and P(OR)<sub>2</sub>; or wherein Z and Z<sub>1</sub> together form the bridging group A-B-A<sub>1</sub>;

wherein each Z', Z'', Z<sub>1</sub>' and Z<sub>1</sub>'' is independently selected from the group consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR<sub>2</sub>,

5 COOR, halide, SiR<sub>3</sub>, P(O)R<sub>2</sub>, P(O)(OR)<sub>2</sub> and P(OR)<sub>2</sub>; or wherein Z' and Z together form the bridging group A'-B-A; Z' and Z together form a fused cycloaliphatic or aromatic group; Z<sub>1</sub> and Z<sub>1</sub>' together form the bridging group A<sub>1</sub>-B<sub>1</sub>-A<sub>1</sub>'; and/or Z<sub>1</sub> and Z<sub>1</sub>' together form a fused cycloaliphatic or aromatic group;

10 wherein each A, A', A<sub>1</sub> and A<sub>1</sub>' is independently selected from the group consisting of: O, CH<sub>2</sub>, NH, NR, S, CO and a bond;

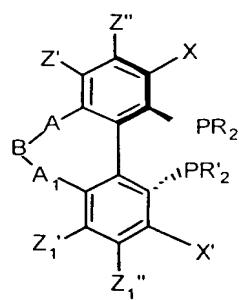
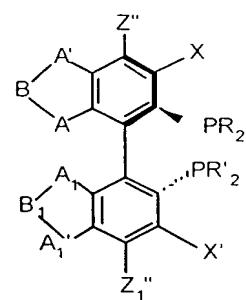
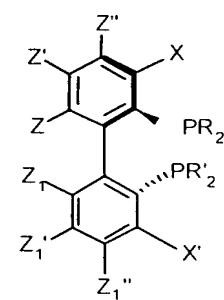
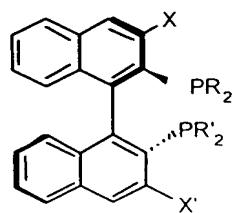
wherein each B and B<sub>1</sub> is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12 carbon atoms, O, CH<sub>2</sub>, NH, NR, S, CO, SO<sub>2</sub>, P(O)R, P(O)OR, POR, SiR<sub>2</sub> and a bond;

15 wherein each YR', YR'', Y'R' and Y''R'' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide and aryloxide; or wherein two YR', YR'', Y'R' or Y''R'' groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

20 wherein each R, R' and R'' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, aralkyl and alkaryl of 1 to 22 carbon atoms; or wherein two R groups, two R' groups or two R'' group together form an alkylene or arelene group; and

25 wherein each Y, Y' and Y'' is independently selected from the group consisting of: O, CH<sub>2</sub>, NH, S and a bond between carbon and phosphorus; with the proviso that when the Y group at the 2' position is a bond between carbon and phosphorus, X' is hydrogen.

14. The ligand of claim 1, wherein said ligand is selected from the  
30 group consisting of compounds represented by the following formulas:



wherein each X is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR<sub>2</sub>, COOR, halide, SiR<sub>3</sub>, P(O)R<sub>2</sub>, P(O)(OR)<sub>2</sub> and P(OR)<sub>2</sub>;

5 wherein each X' is independently selected from the group consisting of: hydrogen, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR<sub>2</sub>, COOR, halide, SiR<sub>3</sub>, P(O)R<sub>2</sub>, P(O)(OR)<sub>2</sub> and P(OR)<sub>2</sub>;

wherein each Z and Z<sub>1</sub> is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR<sub>2</sub>, COOR, halide, SiR<sub>3</sub>, P(O)R<sub>2</sub>, P(O)(OR)<sub>2</sub> and P(OR)<sub>2</sub>;

10 wherein each Z', Z'', Z<sub>1</sub>' and Z<sub>1</sub>'' is independently selected from the group consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR<sub>2</sub>, COOR, halide, SiR<sub>3</sub>, P(O)R<sub>2</sub>, P(O)(OR)<sub>2</sub> and P(OR)<sub>2</sub>;

wherein each A, A', A<sub>1</sub> and A<sub>1</sub>' is independently selected from the group consisting of: O, CH<sub>2</sub>, NH, NR, S, CO and a bond;

15 wherein each B and B<sub>1</sub> is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12 carbon atoms, O, CH<sub>2</sub>, NH, NR, S, CO, SO<sub>2</sub>, P(O)R, P(O)OR, POR, SiR<sub>2</sub> and a bond;

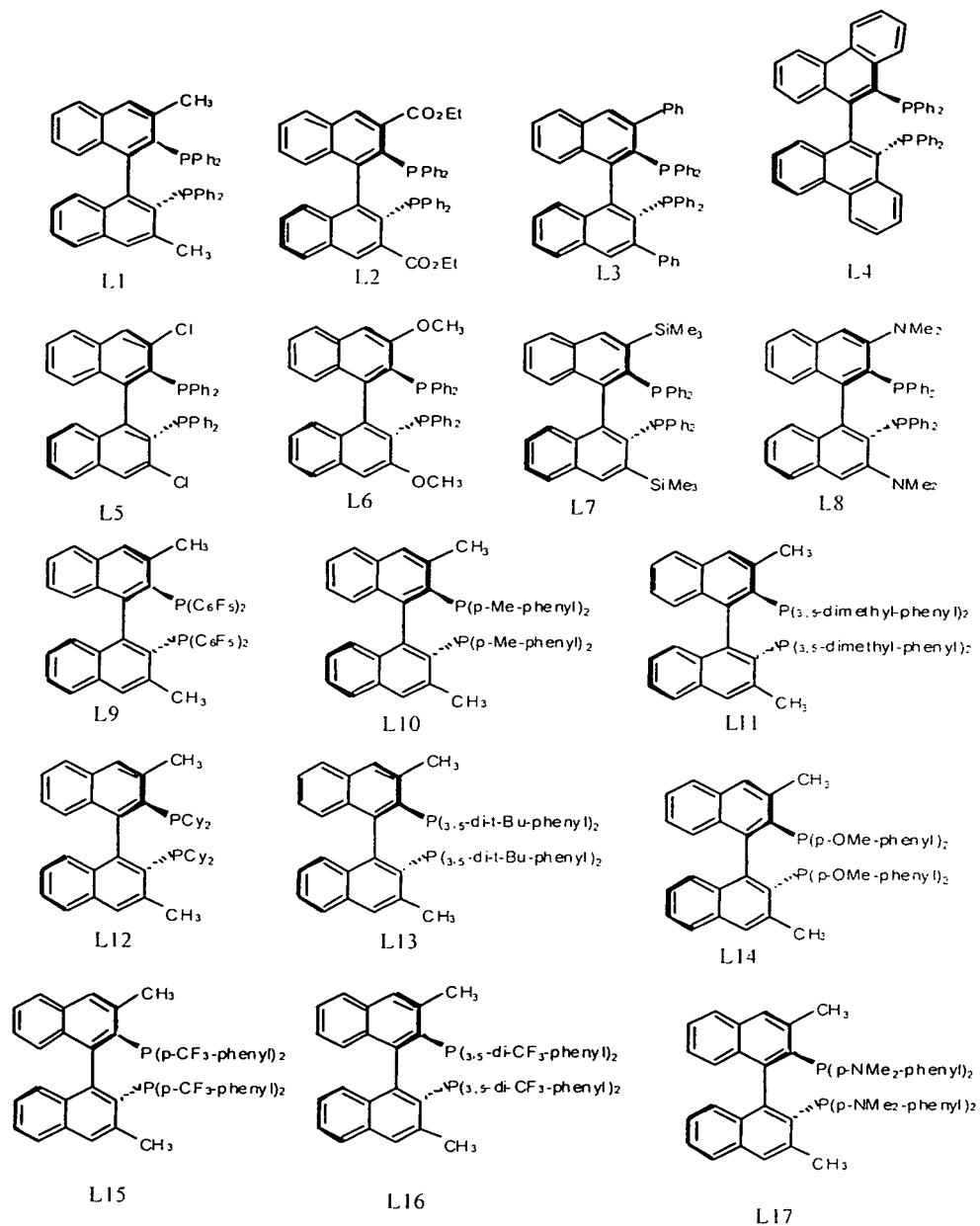
20 wherein each R and R' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, aralkyl and alkaryl of 1 to 22 carbon atoms, alkoxide and aryloxide; or

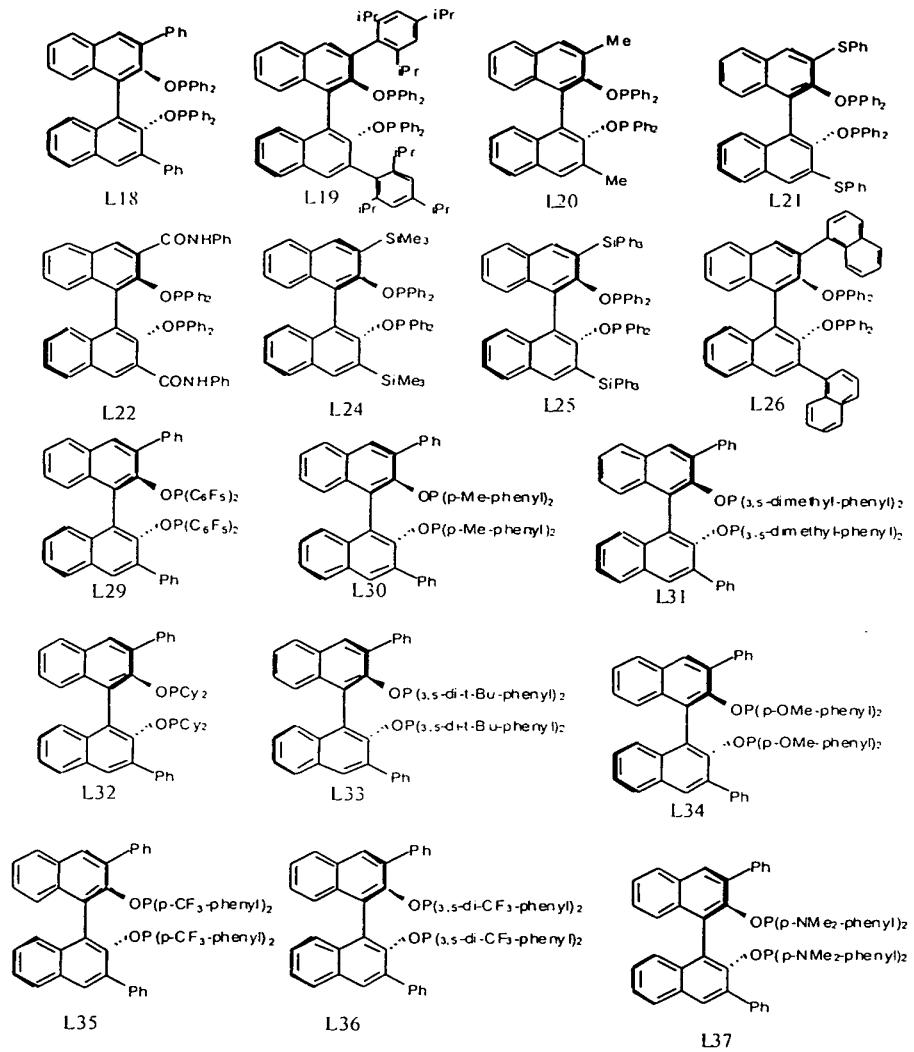
wherein two R groups or two R' groups together form an alkylene, arelene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl groups.

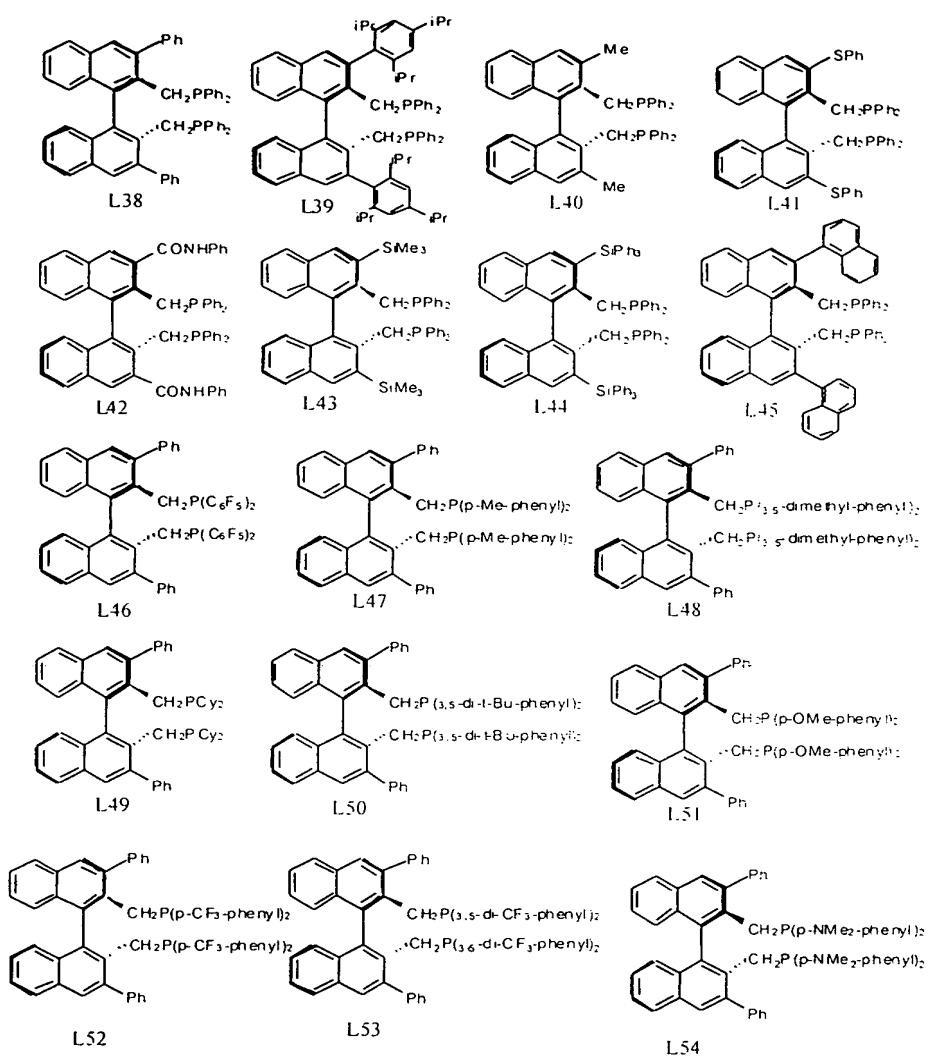
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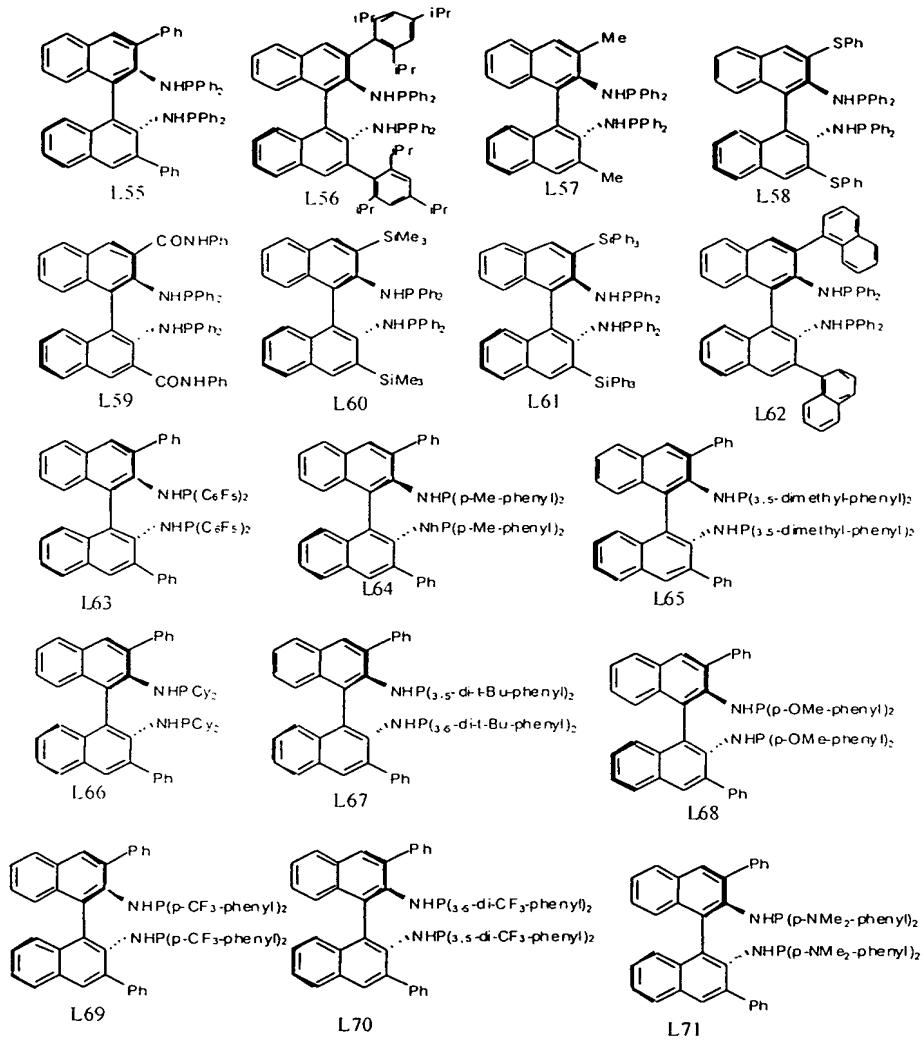
15. The ligand of claim 1, wherein said ligand is selected from the group consisting of compounds represented by the formulas:

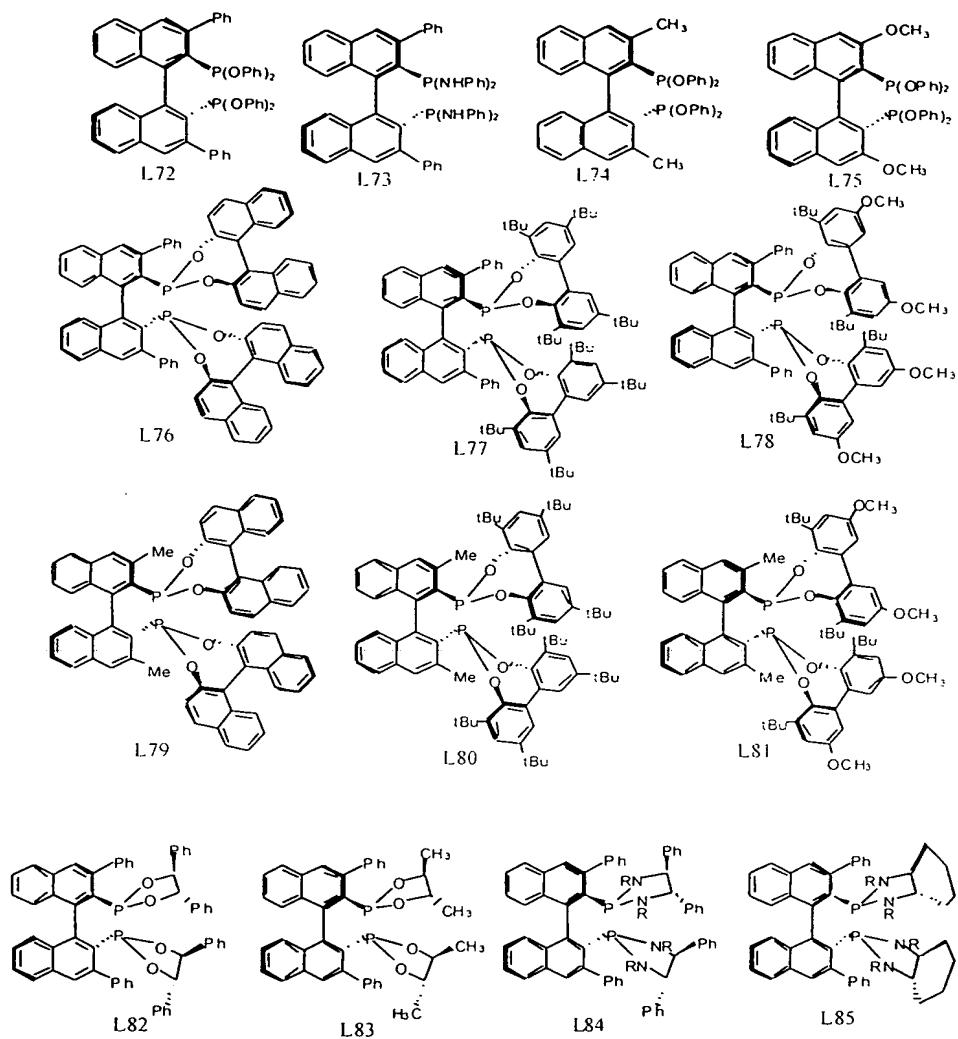
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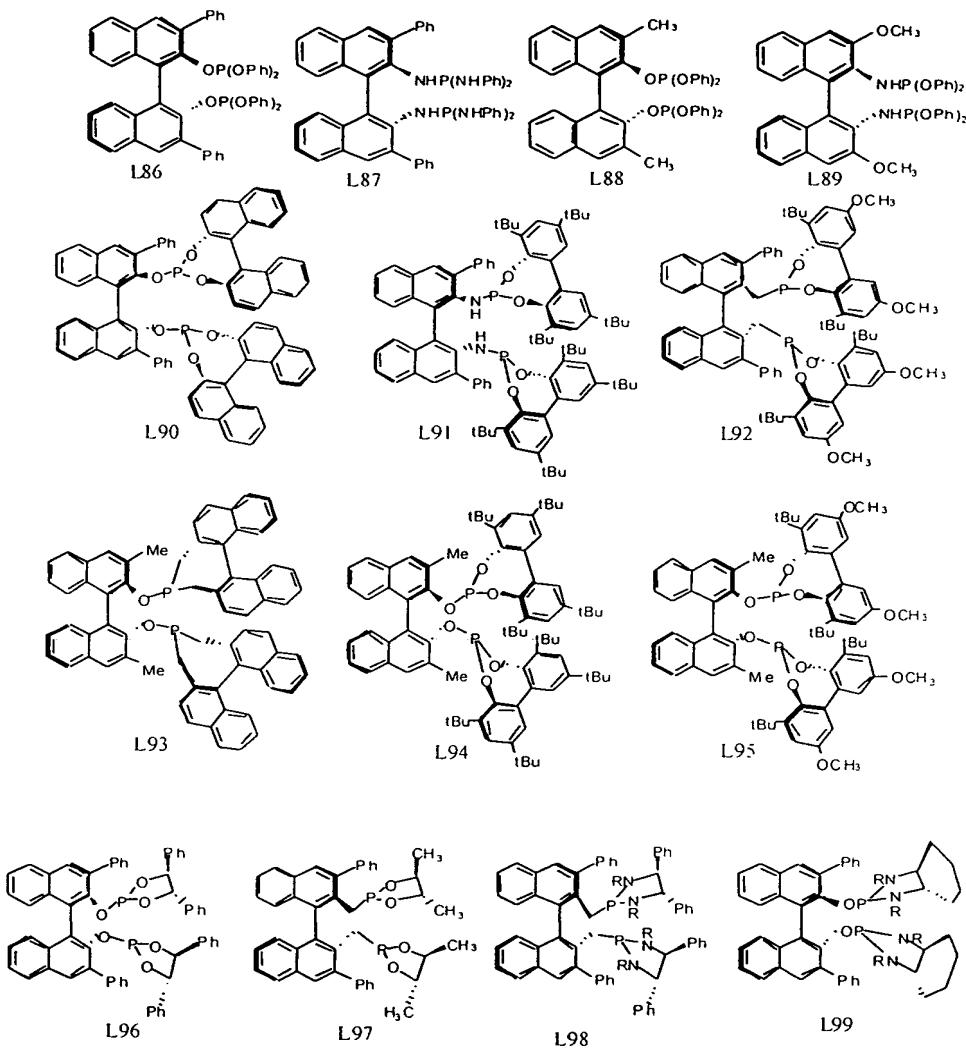


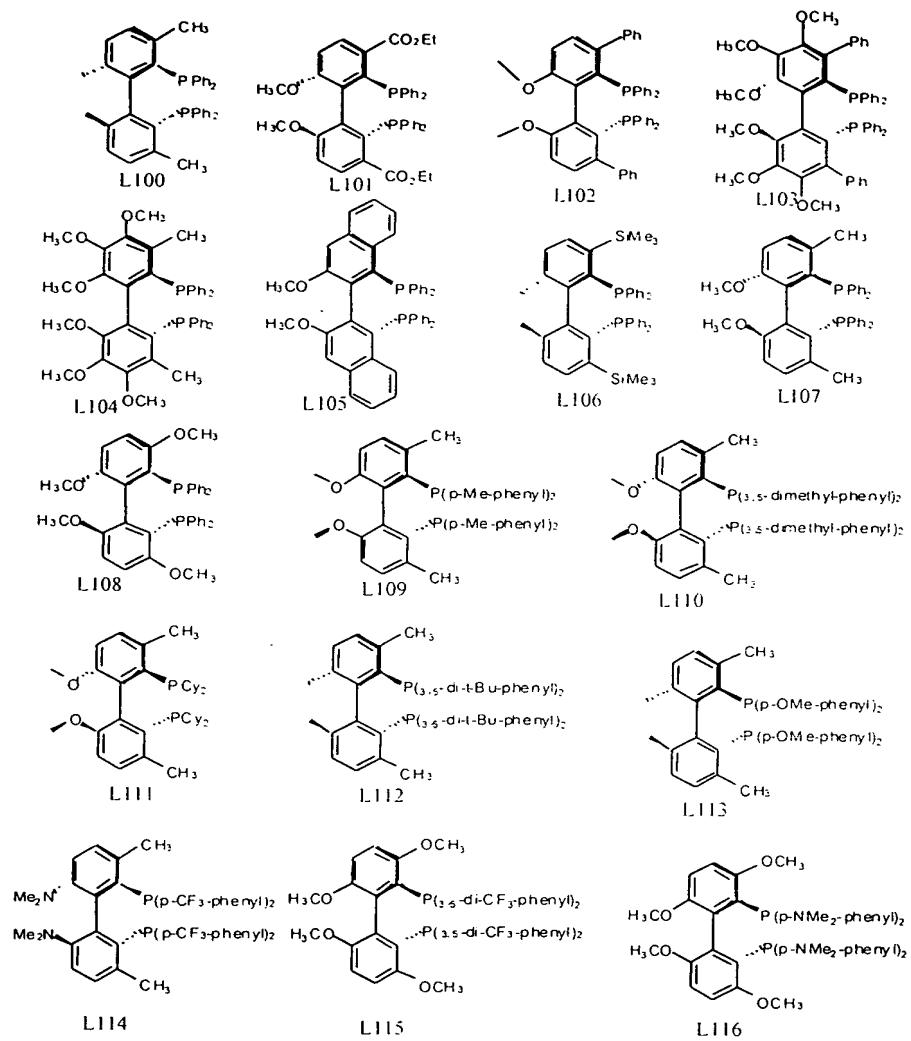


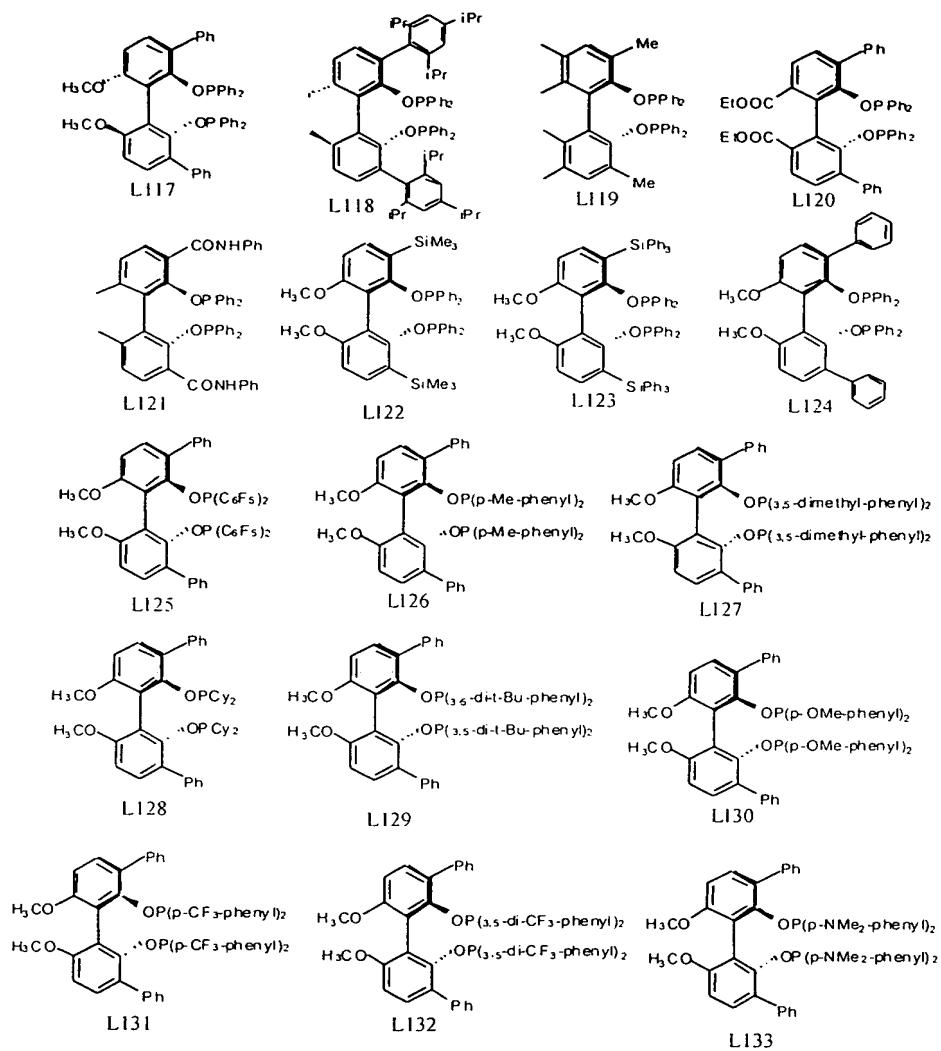


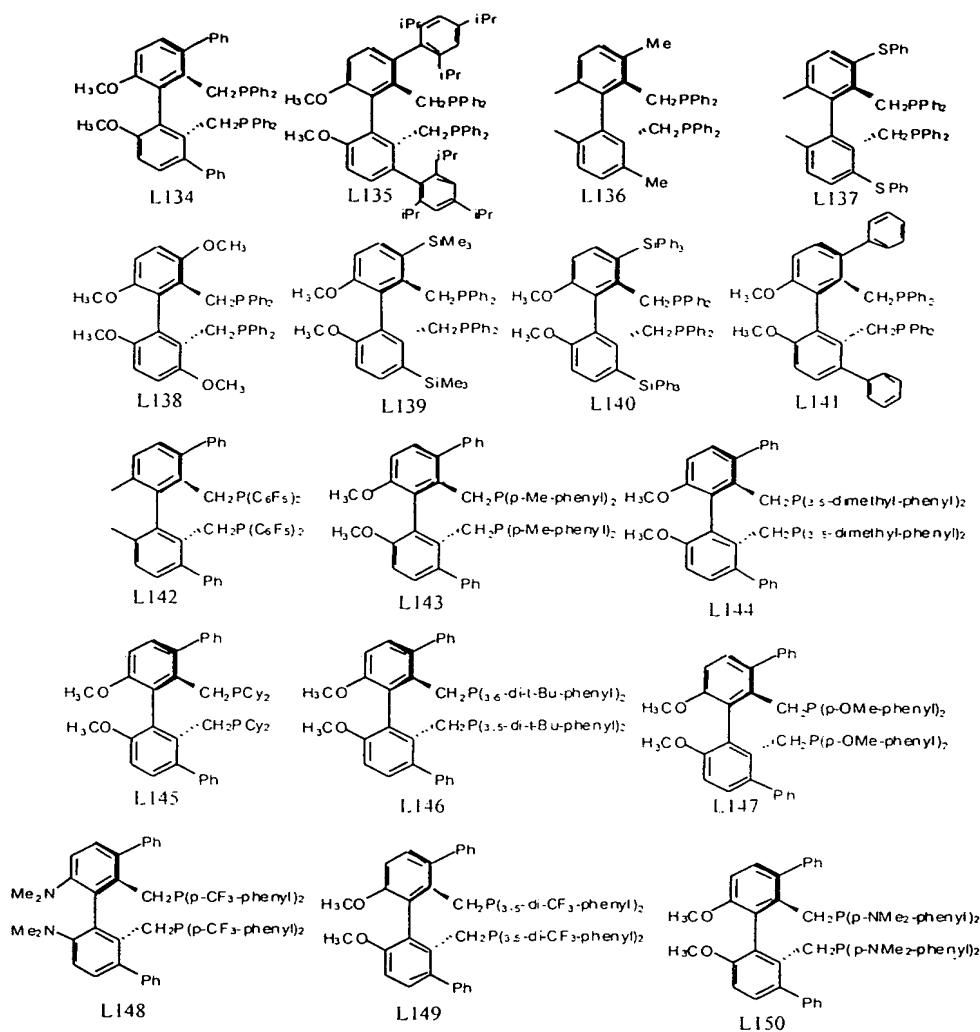


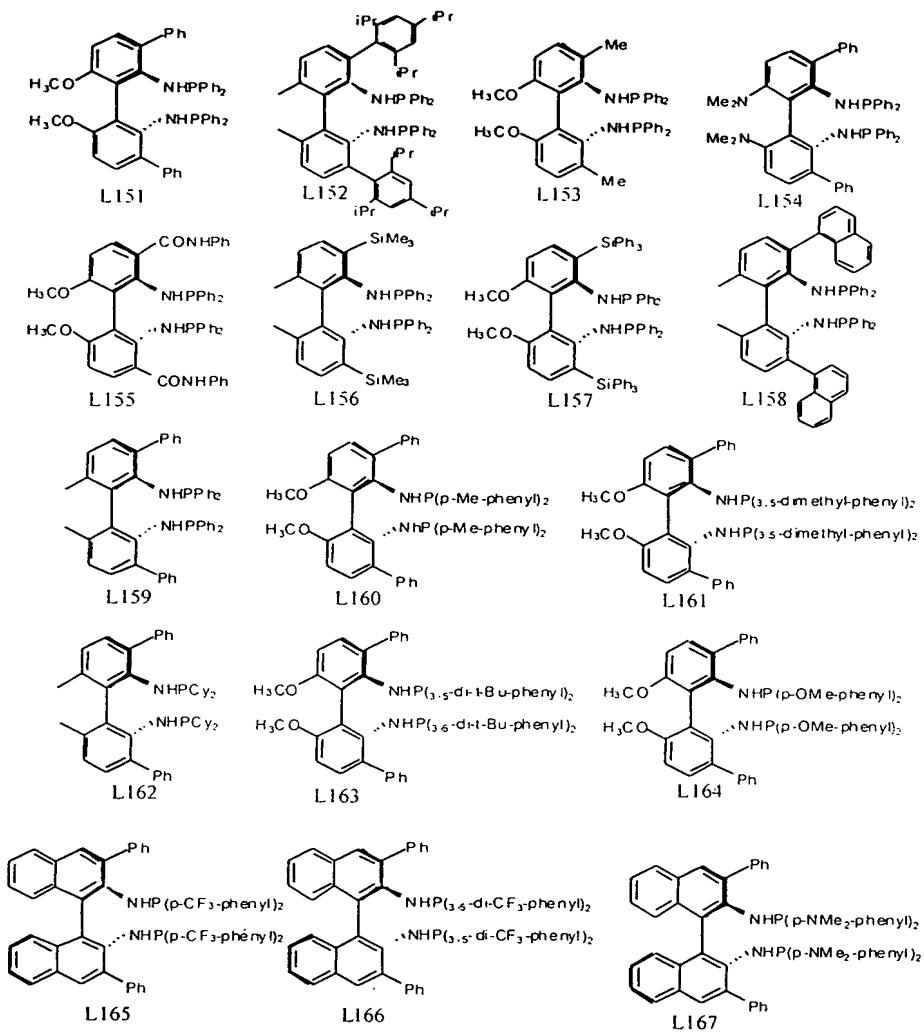


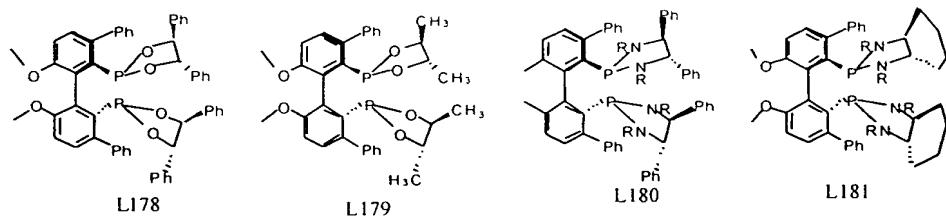
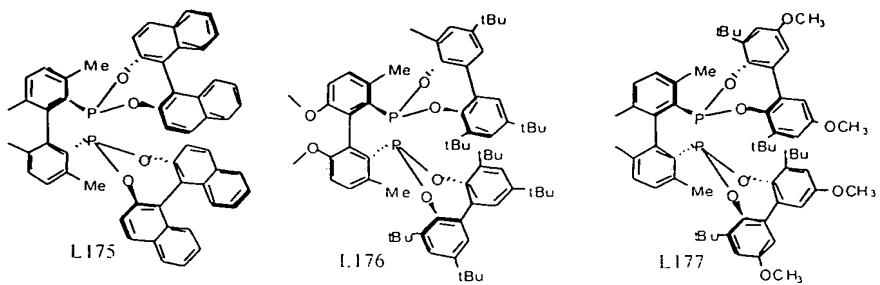
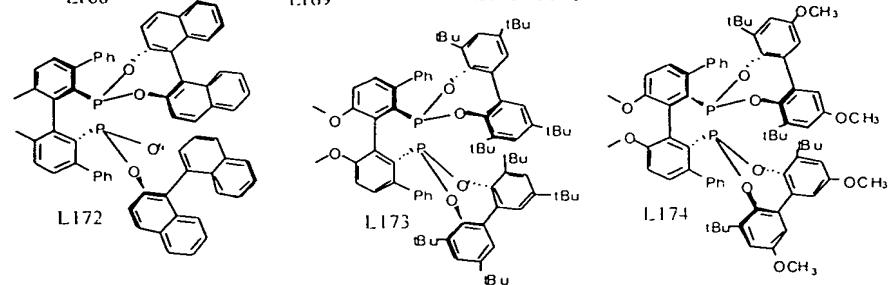
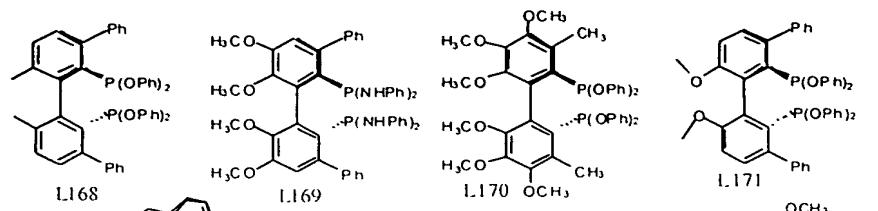


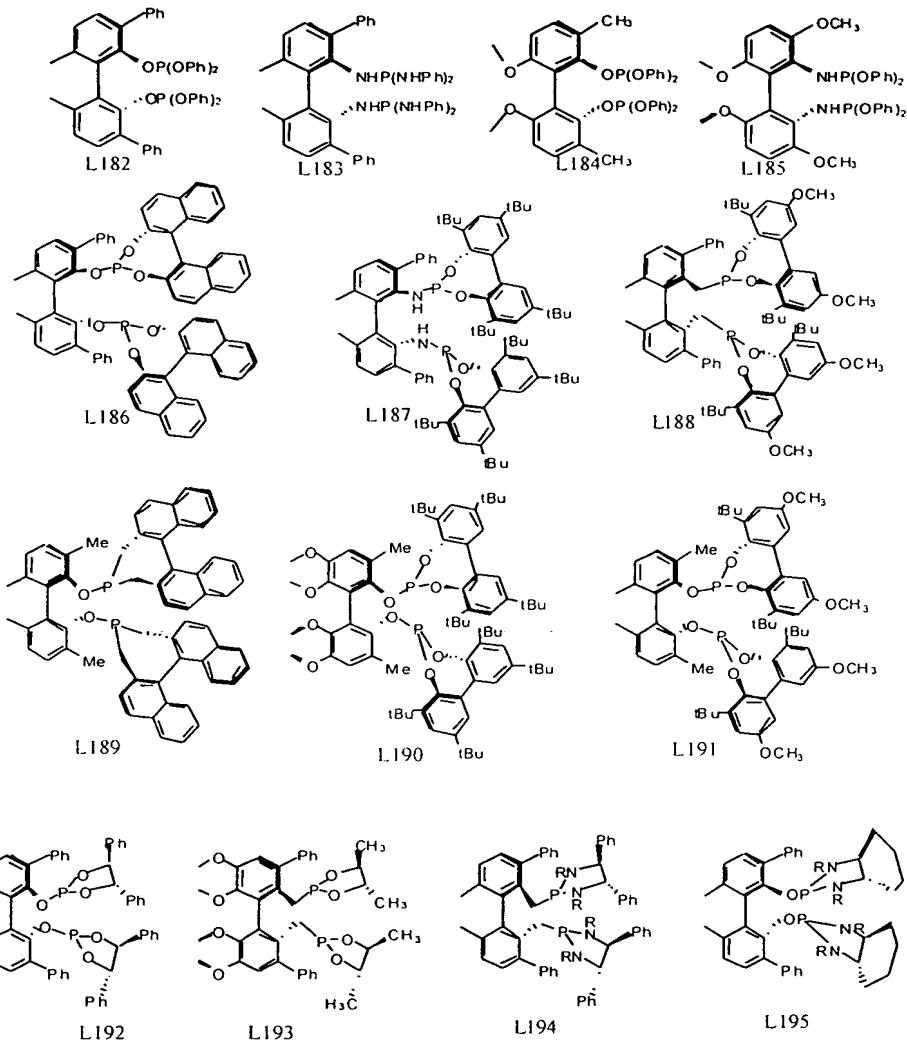


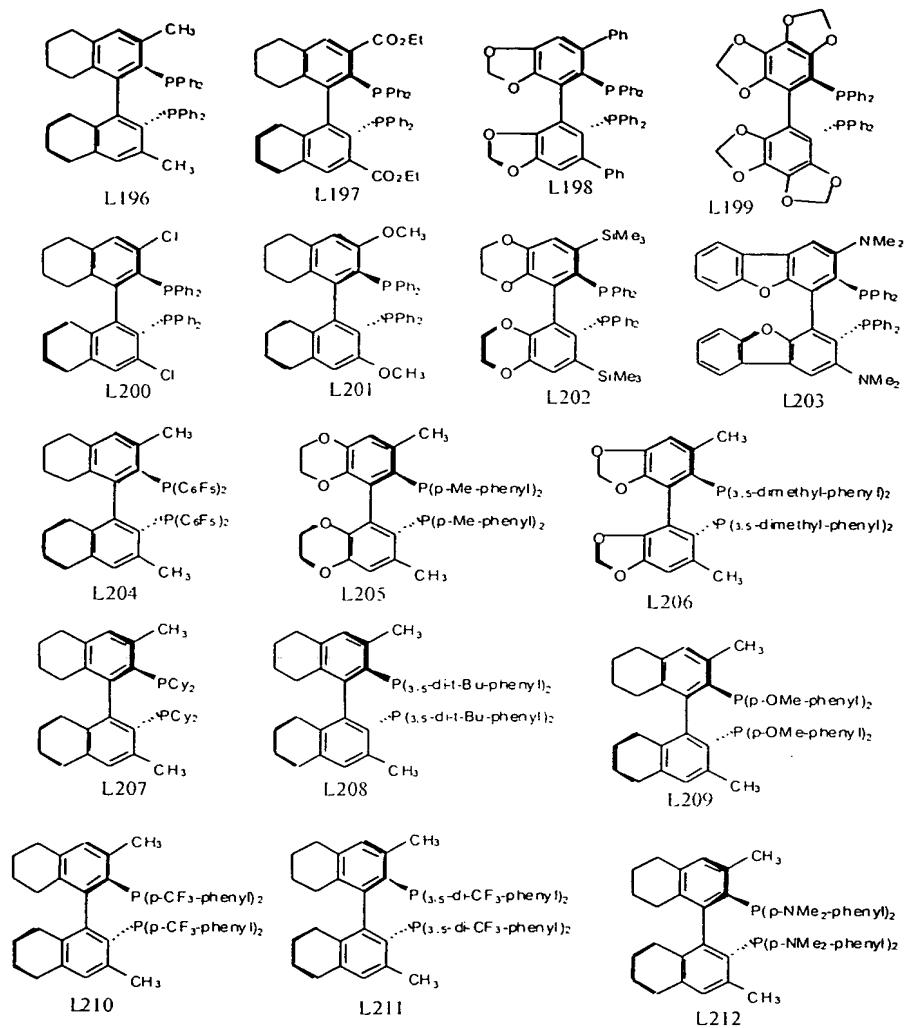


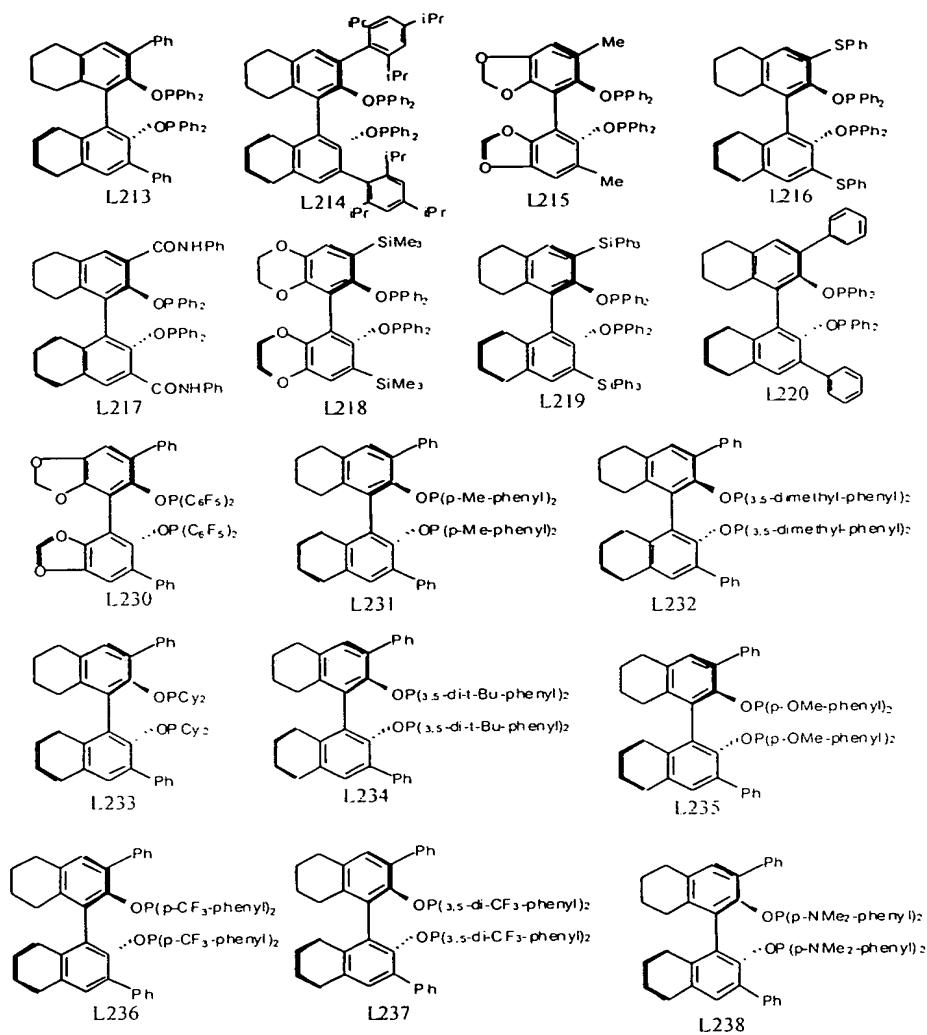


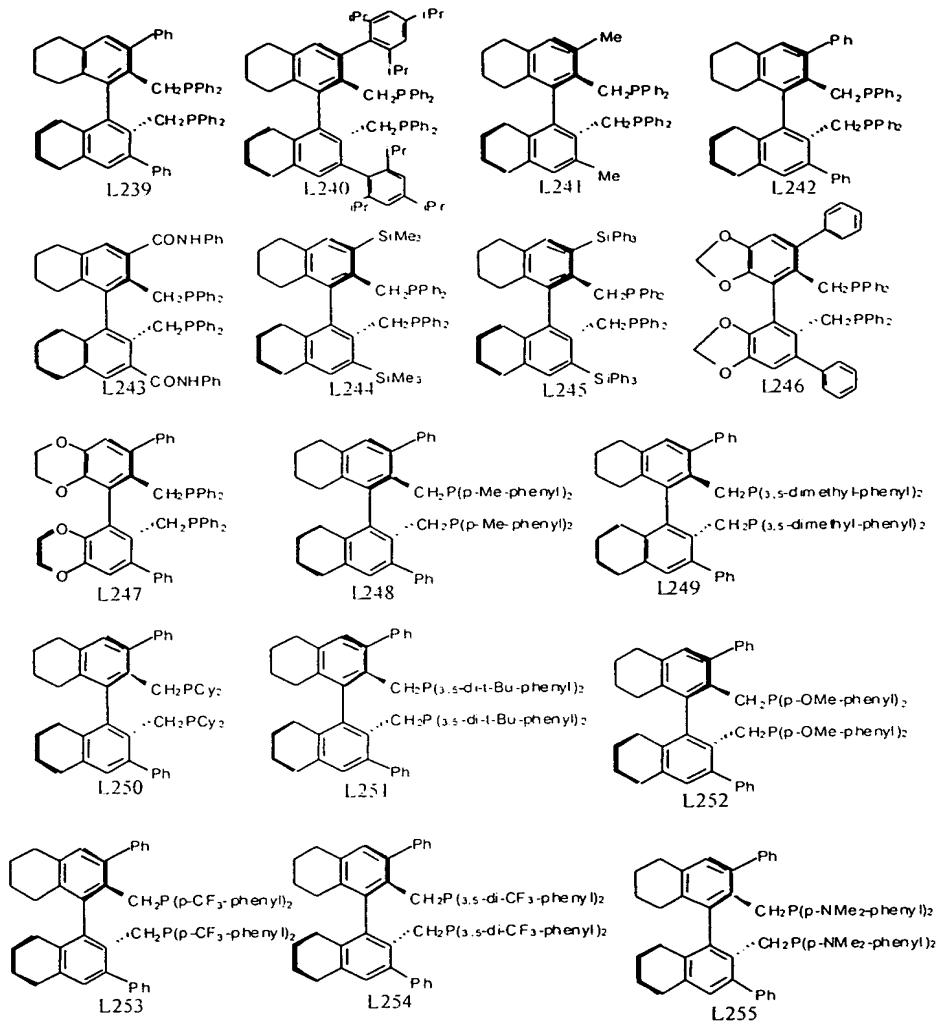


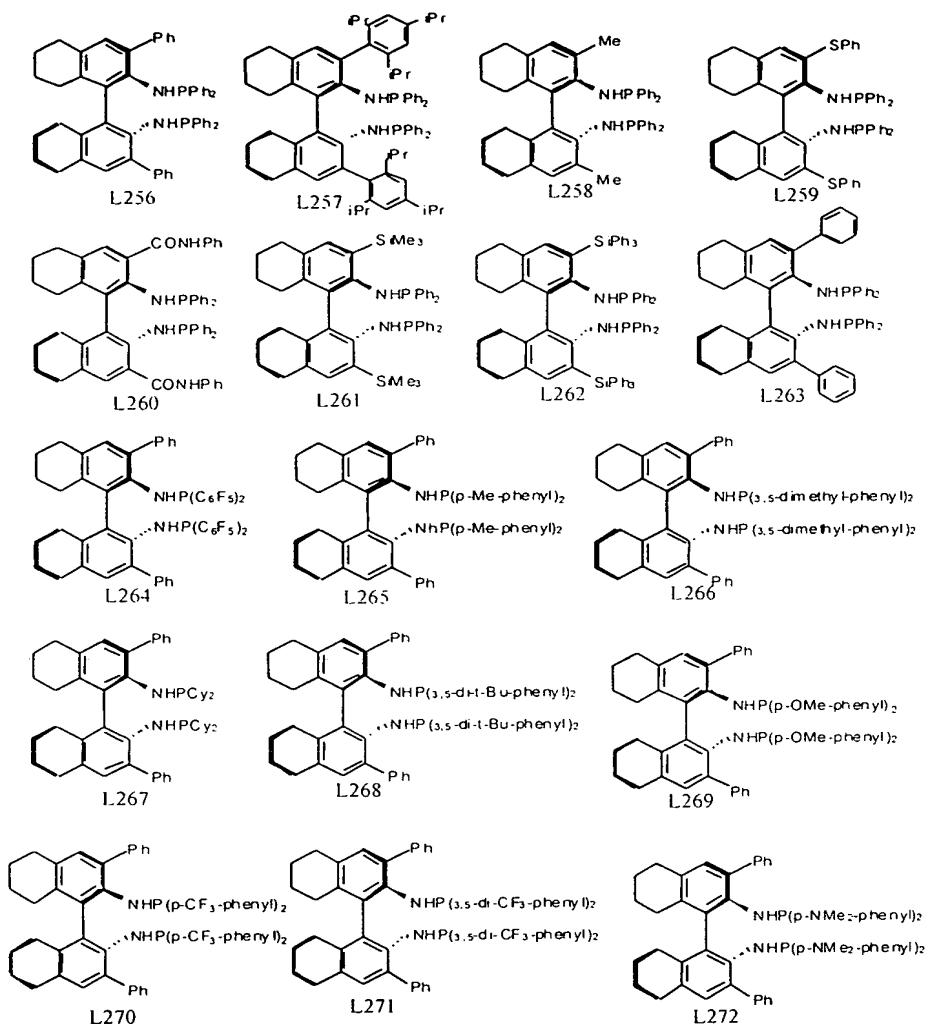


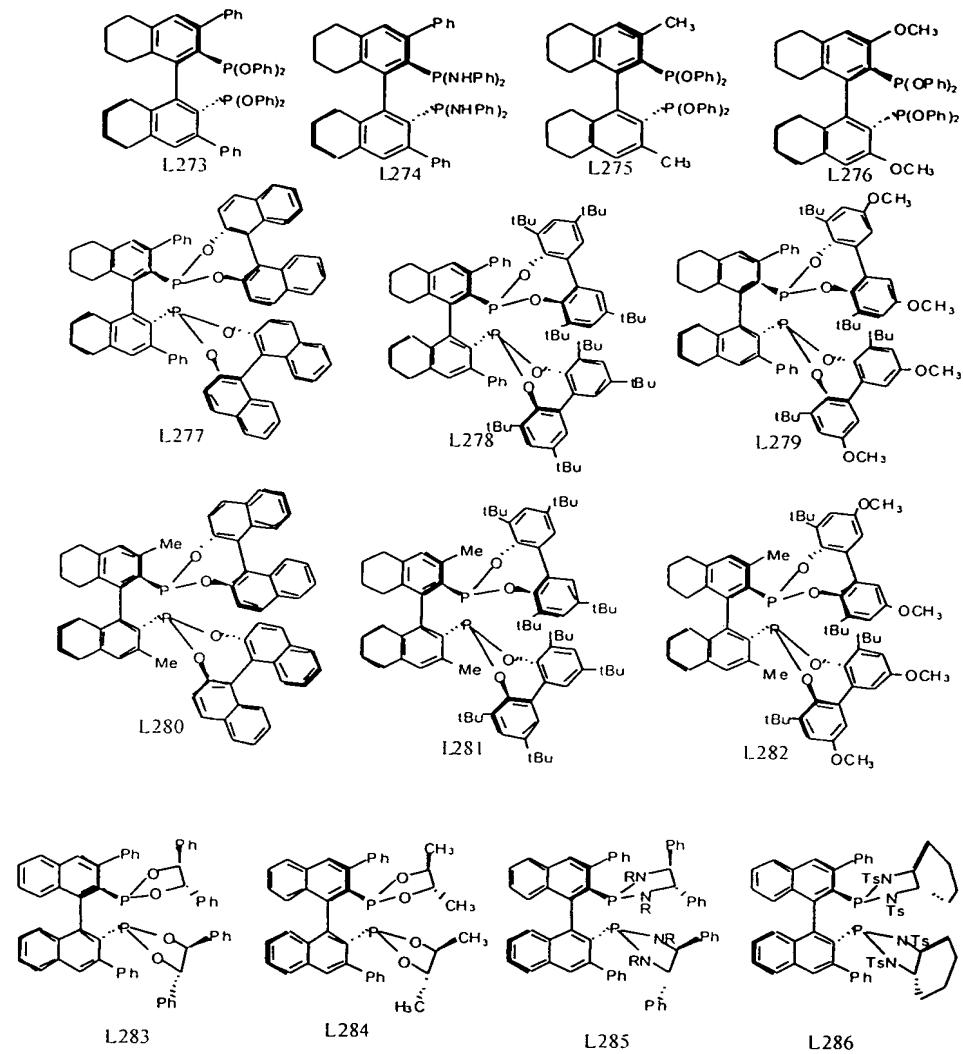


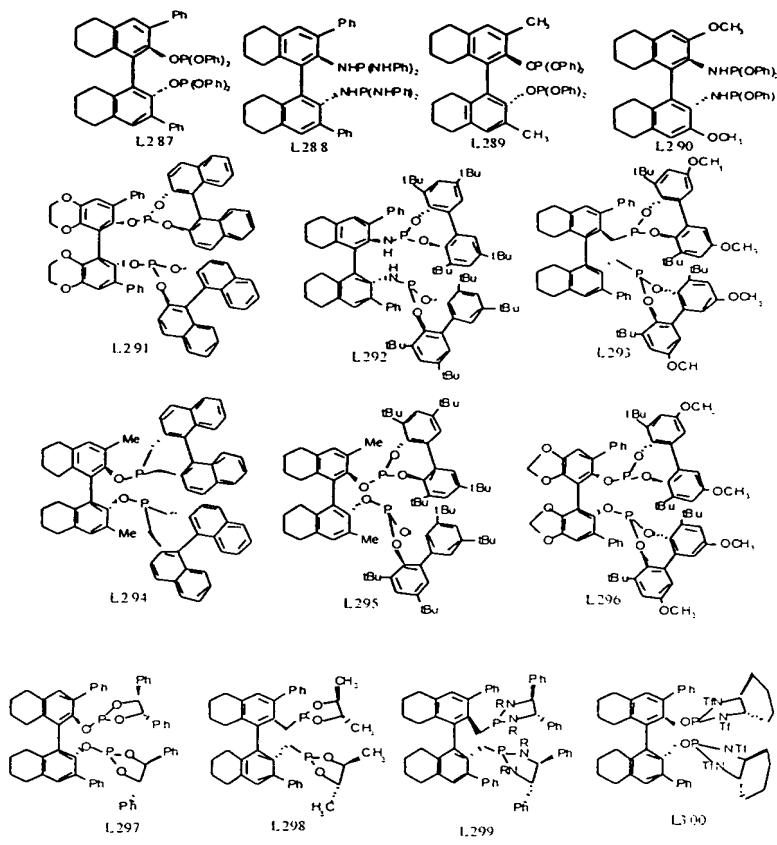


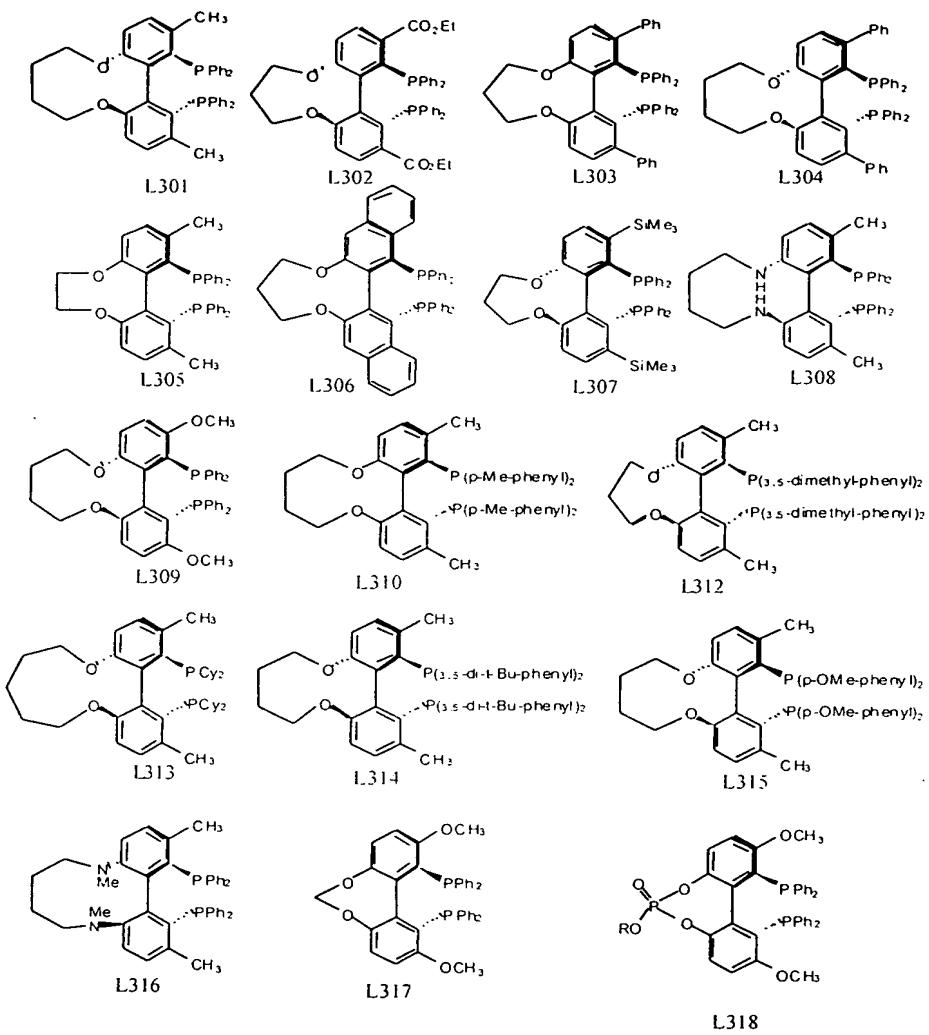


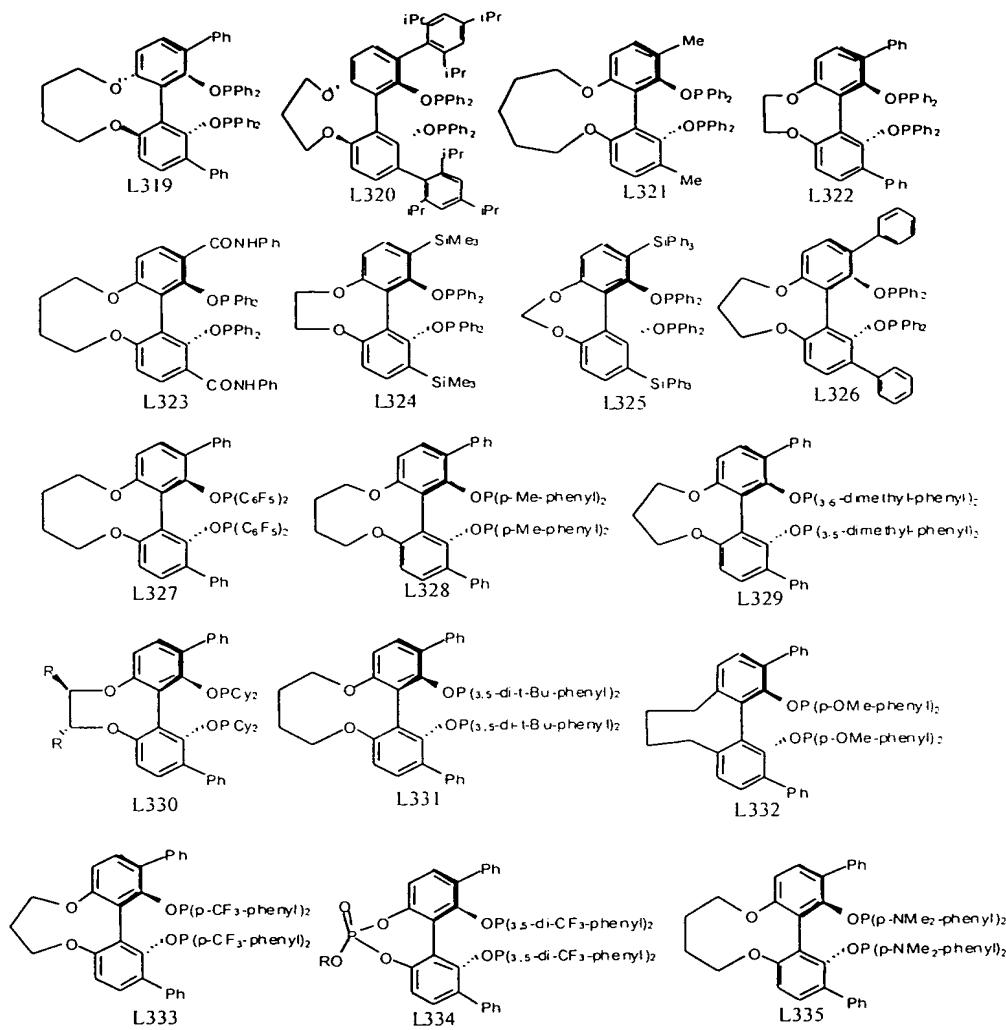


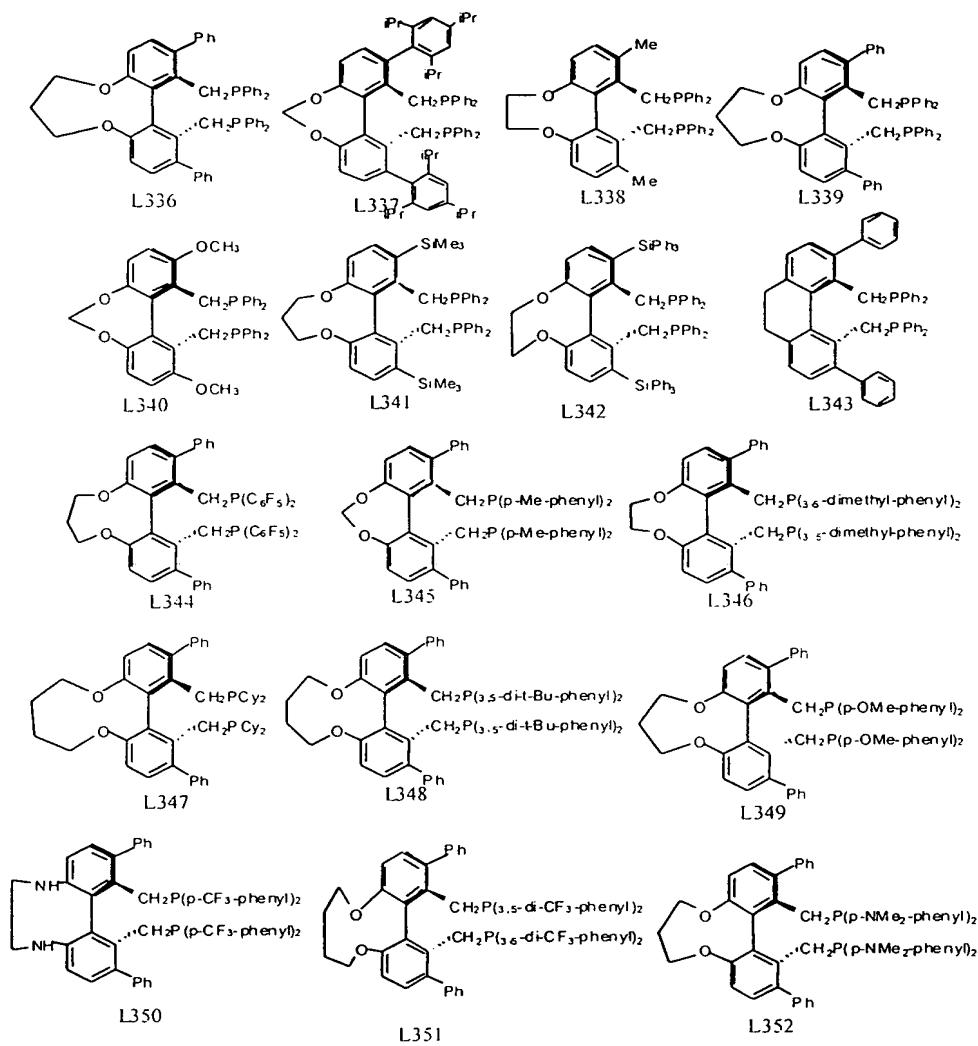


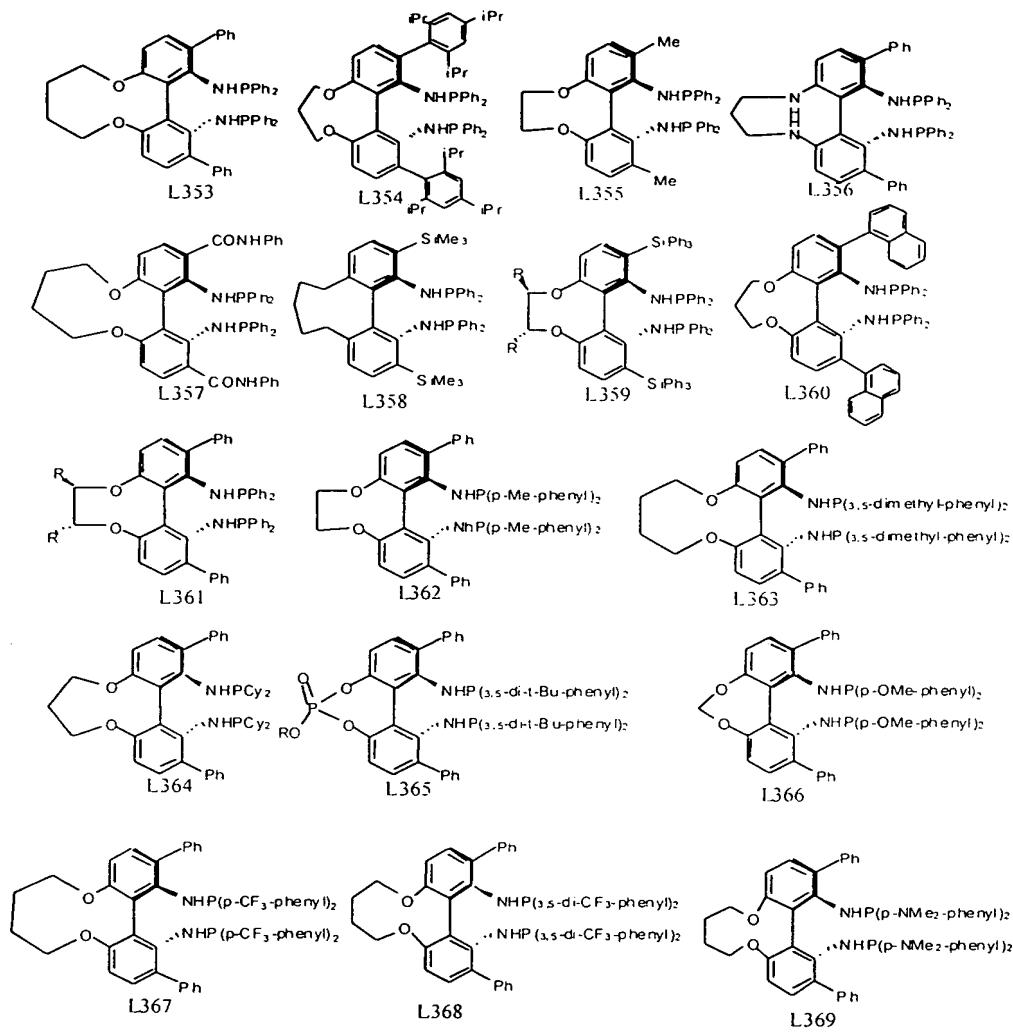


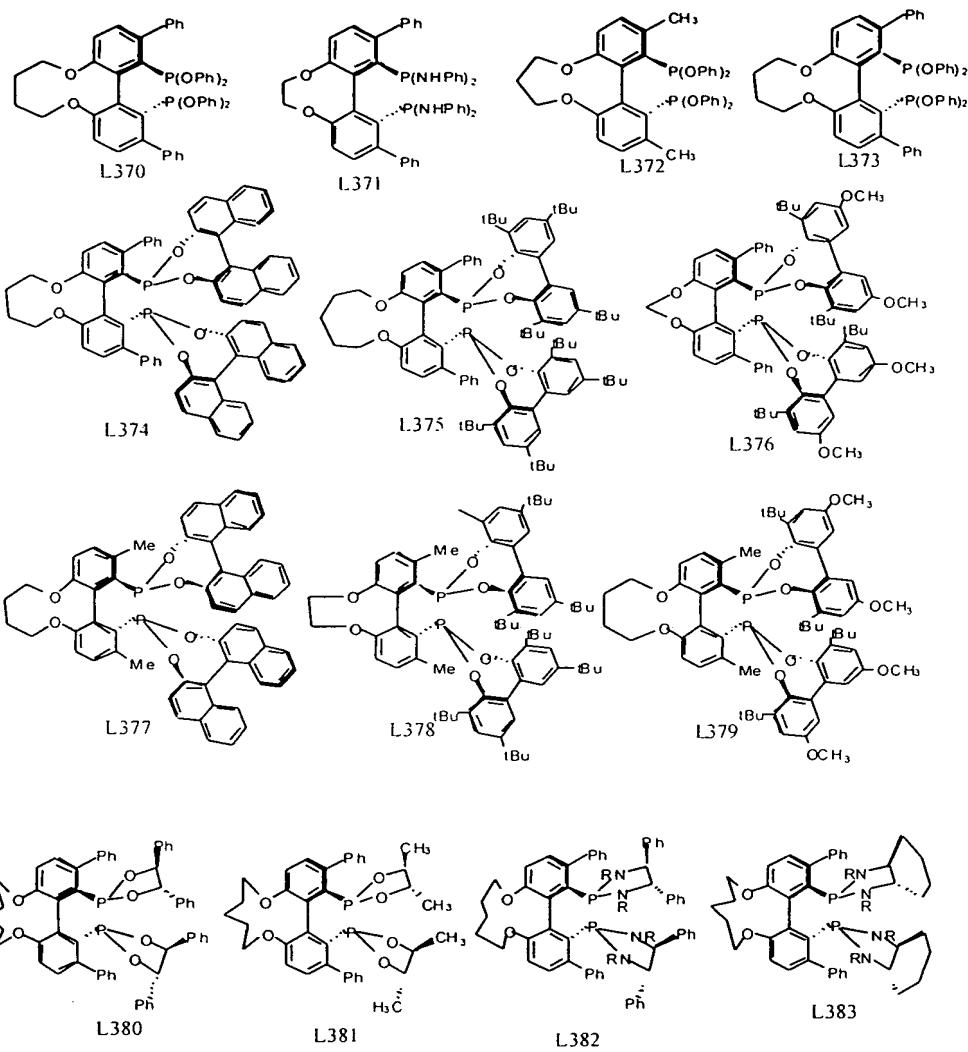


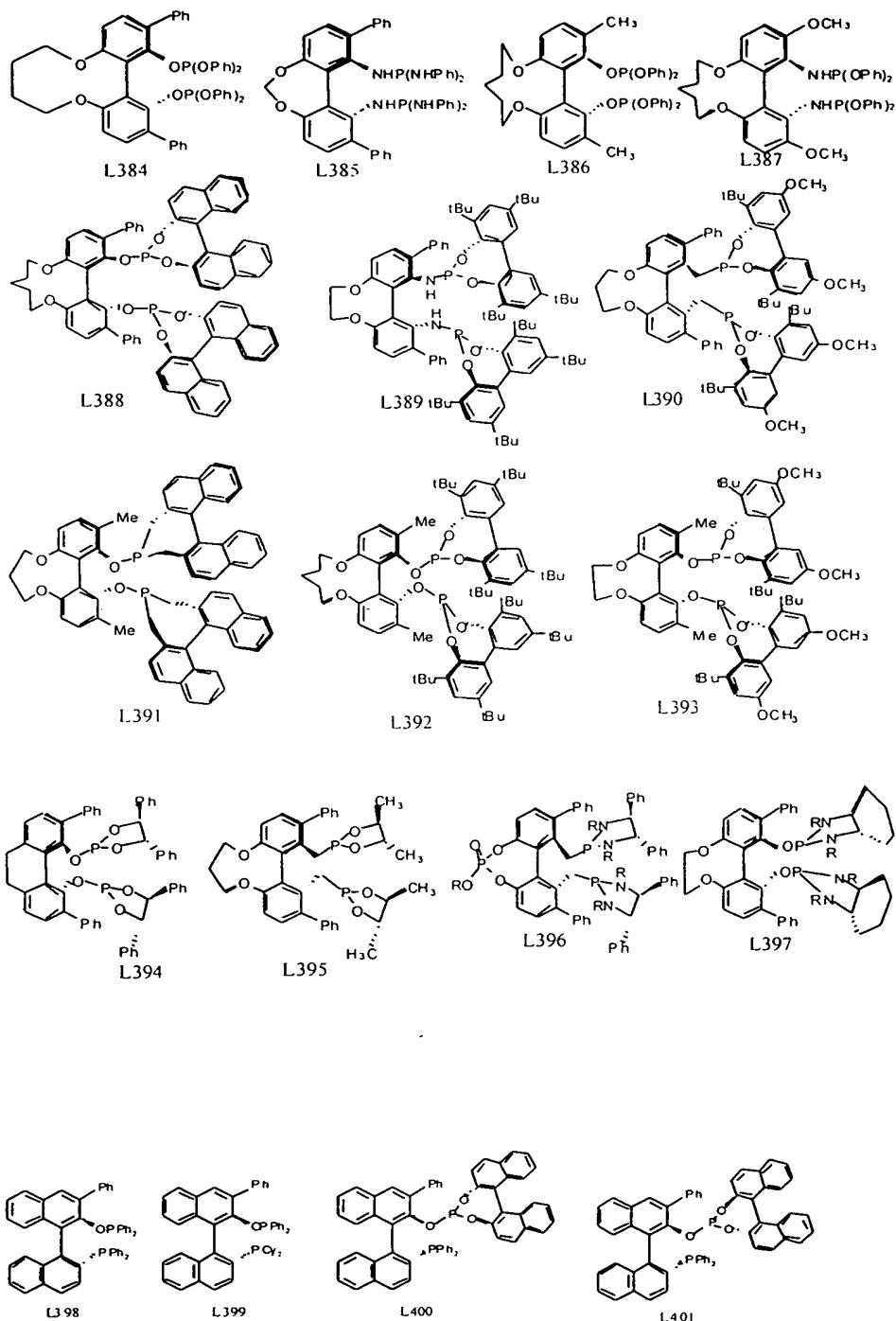




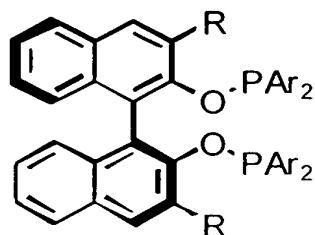




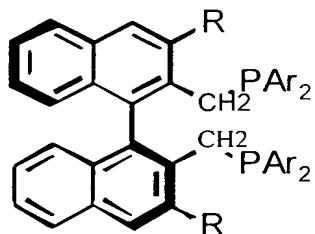




16. The ligand of claim 1, represented by the formula:



or

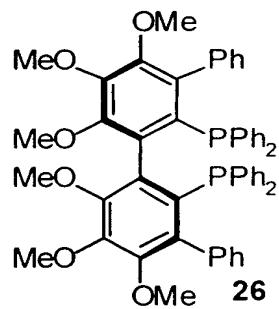


wherein each R is independently selected from the group consisting of:

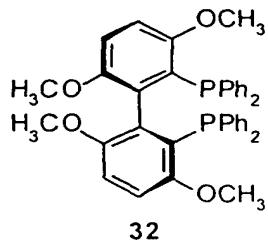
5 alkyl, aryl, substituted alkyl, substituted aryl and SiR<sub>3</sub>; and wherein each Ar is independently selected from the group consisting of: phenyl, substituted phenyl, aryl and substituted aryl.

17. The ligand of claim 1, represented by the formula:

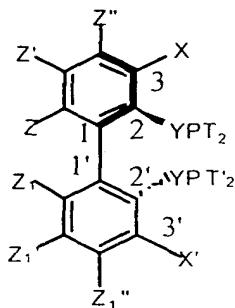
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18. The ligand of claim 1, represented by the formula:



19. A catalyst prepared by a process comprising:  
 contacting a transition metal salt, or a complex thereof, and a ligand  
 5 selected from the group consisting of compounds represented by the formula or its  
 enantiomer:



wherein each X and X' is independently selected from the group  
 consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR2, COOR,  
 10 halide, SiR3, P(O)R2, P(O)(OR)2 and P(OR)2;  
 wherein each Z and Z1 is independently selected from the group consisting  
 of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR2, COOR, halide,  
 SiR3, P(O)R2, P(O)(OR)2 and P(OR)2; or wherein Z and Z1 together form the  
 bridging group A-B-A1;  
 15 wherein each Z', Z'', Z1' and Z1'' is independently selected from the group  
 consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR2,  
 COOR, halide, SiR3, P(O)R2, P(O)(OR)2 and P(OR)2; or wherein Z' and Z  
 together form the bridging group A'-B-A; Z' and Z together form a fused  
 cycloaliphatic or aromatic group; Z1 and Z1' together form the bridging group A1-  
 20 B1-A1'; and/or Z1 and Z1' together form a fused cycloaliphatic or aromatic group;

wherein each A, A', A<sub>1</sub> and A<sub>1</sub>' is independently selected from the group consisting of: O, CH<sub>2</sub>, NH, NR, S, CO and a bond;

wherein each B and B<sub>1</sub> is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12 carbon atoms, O, CH<sub>2</sub>, NH, NR, S, CO, SO<sub>2</sub>, P(O)R, P(O)OR, POR, SiR<sub>2</sub> and a bond;

wherein each T is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R'', YR', YR'', Y'R' and Y''R'; or wherein two T groups together form an alkylene, arylene, alkylidendiamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each T' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R'', YR', YR'', Y'R' and Y''R'; or wherein two T' groups together form an alkylene, arylene, alkylidendiamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each R, R' and R'' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, aralkyl and alkaryl of 1 to 22 carbon atoms; or wherein two R groups, two R' groups or two R'' group together form an alkylene or arelene group; and

wherein each Y, Y' and Y'' is independently selected from the group consisting of: O, CH<sub>2</sub>, NH, S and a bond between carbon and phosphorus; with the proviso that when the Y group at the 2' position is a bond between carbon and phosphorus, X' is hydrogen.

20. The catalyst of claim 19, wherein said substituted alkyl has one or more substituents, each independently selected from the group consisting of: halogen, ester, ketone, carboxylic acid, hydroxy, alkoxy, aryloxy, thiol, alkylthio and dialkylamino.

21. The catalyst of claim 19, wherein said alkylene is selected from the group consisting of compounds represented by the formula: -(CH<sub>2</sub>)<sub>n</sub>-, where n is an integer in the range of from 1 to 8.

22. The catalyst of claim 19, wherein each of said aryl groups  
optionally has one or more substituents, each independently selected from the  
group consisting of: halogen, ester, ketone, sulfonate, phosphonate, hydroxy,  
alkoxy, aryloxy, thiol, alkylthiol, nitro, amino, vinyl, substituted vinyl, carboxylic  
acid, sulfonic acid and phosphine.

5

23. The catalyst of claim 19, wherein each of said arylene groups  
optionally has one or more substituents, each independently selected from the  
group consisting of: halogen, ester, ketone, sulfonate, phosphonate, hydroxy,  
10 alkoxy, aryloxy, thiol, alkylthiol, nitro, amino, vinyl, substituted vinyl, carboxylic  
acid, sulfonic acid and phosphine.

15

24. The catalyst of claim 19, wherein each of said arylene groups is  
independently selected from the group consisting of: 1,2-divalent phenyl, 2,2'-  
divalent-1,1'-biphenyl, 2,2'-divalent-1,1'-binaphthyl and ferrocene.

20

25. The catalyst of claim 19, wherein said ligand is a racemic mixture  
of enantiomers.

26. The catalyst of claim 19, wherein said ligand is a non-racemic  
mixture of enantiomers.

25

27. The catalyst of claim 19, wherein said ligand is one of the  
enantiomers.

28. The catalyst of claim 19, having an optical purity of at least 85%  
ee.

29. The catalyst of claim 19, having an optical purity of at least 95%  
30 ee.

30. The catalyst of claim 19, wherein said transition metal is selected from the group consisting of: Ag, Pt, Pd, Rh, Ru, Ir, Cu, Ni, Mo, Ti, V, Re and Mn.

5 31. The catalyst of claim 19, wherein said transition metal is selected from the group consisting of: Pt, Pd, Rh and Ru.

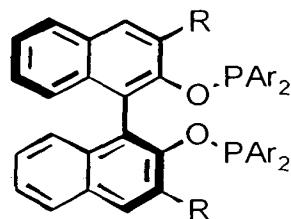
32. The catalyst of claim 19, wherein said transition metal salt, or complex thereof, is selected from the group consisting of: AgX; Ag(OTf);  
10 Ag(OTf)<sub>2</sub>; AgOAc; PtCl<sub>2</sub>; H<sub>2</sub>PtCl<sub>4</sub>; Pd<sub>2</sub>(DBA)<sub>3</sub>; Pd(OAc)<sub>2</sub>; PdCl<sub>2</sub>(RCN)<sub>2</sub>; (Pd(allyl)Cl)<sub>2</sub>; Pd(PR<sub>3</sub>)<sub>4</sub>; (Rh(NBD)<sub>2</sub>)X; (Rh (NBD)Cl)<sub>2</sub>; (Rh(COD)Cl)<sub>2</sub>; (Rh(COD)<sub>2</sub>)X; Rh(acac)(CO)<sub>2</sub>; Rh(ethylene)<sub>2</sub>(acac); (Rh(ethylene)<sub>2</sub>Cl)<sub>2</sub>; RhCl(PPh<sub>3</sub>)<sub>3</sub>; Rh(CO)<sub>2</sub>Cl<sub>2</sub>; RuHX(L)<sub>2</sub>(diphosphine), RuX<sub>2</sub>(L)<sub>2</sub> (diphosphine), Ru(arene)X<sub>2</sub>(diphosphine), Ru(aryl group)X<sub>2</sub>; Ru(RCOO)<sub>2</sub>(diphosphine);  
15 Ru(methallyl)2(diphosphine); Ru(aryl group)X<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>; Ru(COD)(COT); Ru(COD)(COT)X; RuX<sub>2</sub>(cymen); Ru(COD)<sub>n</sub>; Ru(aryl group)X<sub>2</sub>(diphosphine); RuCl<sub>2</sub>(COD); (Ru(COD)<sub>2</sub>)X; RuX<sub>2</sub>(diphosphine); RuCl<sub>2</sub>(=CHR)(PR'<sub>3</sub>)<sub>2</sub>; Ru(ArH)Cl<sub>2</sub>; Ru(COD)(methallyl)<sub>2</sub>; (Ir (NBD)<sub>2</sub>Cl)<sub>2</sub>; (Ir(NBD)<sub>2</sub>)X; (Ir(COD)<sub>2</sub>Cl)<sub>2</sub>; (Ir(COD)<sub>2</sub>)X; CuX (NCCH<sub>3</sub>)<sub>4</sub>; Cu(OTf); Cu(OTf)<sub>2</sub>; Cu(Ar)X; CuX; Ni(acac)<sub>2</sub>;  
20 NiX<sub>2</sub>; (Ni(allyl)X)<sub>2</sub>; Ni(COD)<sub>2</sub>; MoO<sub>2</sub>(acac)<sub>2</sub>; Ti(OiPr)<sub>4</sub>; VO(acac)<sub>2</sub>; MeReO<sub>3</sub>; MnX<sub>2</sub> and Mn(acac)<sub>2</sub>; wherein each R and R' is independently selected from the group consisting of: alkyl or aryl; Ar is an aryl group; and X is a counteranion.

25 33. The catalyst of claim 32, wherein L is a solvent molecule and wherein said counteranion X is selected from the group consisting of: halogen, BF<sub>4</sub>, B(Ar)4, wherein Ar is fluorophenyl or 3,5-di-trifluoromethyl-1-phenyl, ClO<sub>4</sub>, SbF<sub>6</sub>, PF<sub>6</sub>, CF<sub>3</sub>SO<sub>3</sub>, RCOO and a mixture thereof.

30 34. The catalyst of claim 19, prepared in situ or as an isolated compound.

35. The catalyst of claim 19, wherein said transition metal salt, or a complex thereof is selected from the group consisting of:  $[\text{Rh}(\text{COD})\text{Cl}]_2$ ,  $[\text{Rh}(\text{COD})_2]\text{X}$ ,  $[\text{Ir}(\text{COD})\text{Cl}]_2$ ,  $[\text{Ir}(\text{COD})_2]\text{X}$ ,  $\text{Rh}(\text{acac})(\text{CO})_2$ ,  $\text{Ni}(\text{allyl})\text{X}$ ,  $\text{Pd}_2(\text{dba})_3$ ,  $[\text{Pd}(\text{allyl})\text{Cl}]_2$ ,  $\text{Ru}(\text{RCOO})_2(\text{diphosphine})$ ,  $\text{RuX}_2(\text{diphosphine})$ , 5  $\text{Ru}(\text{methylallyl})_2(\text{diphosphine})$  and  $\text{Ru}(\text{aryl})\text{X}_2(\text{diphosphine})$ , wherein X is selected from the group consisting of:  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{SbF}_6^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{Cl}$  and  $\text{Br}$ ; and wherein said ligand is selected from the group consisting of compounds represented by the formula:

(a)

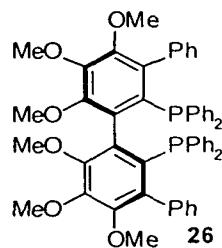


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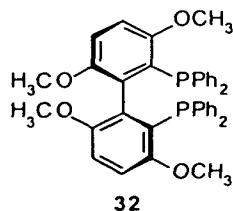
wherein each R is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl and  $\text{SiR}_3$ ; and wherein each Ar is independently selected from the group consisting of: phenyl, substituted phenyl, aryl and substituted aryl;

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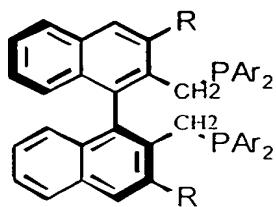
(b)



(c)

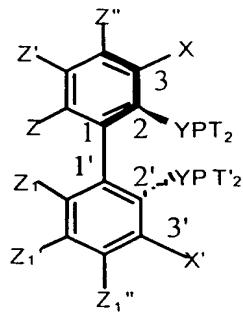


(d)



5 and a combination thereof.

36. A process for preparation of an asymmetric compound comprising:  
contacting a substrate capable of forming an asymmetric product by an  
asymmetric reaction and a catalyst prepared by a process comprising: contacting a  
10 transition metal salt, or a complex thereof, and a ligand selected from the group  
consisting of compounds represented by the formula or its enantiomer:



15

wherein each X and X' is independently selected from the group  
consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR2, COOR,  
halide, SiR3, P(O)R2, P(O)(OR)2 and P(OR)2;

wherein each Z and Z1 is independently selected from the group consisting  
20 of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR2, COOR, halide,

SiR<sub>3</sub>, P(O)R<sub>2</sub>, P(O)(OR)<sub>2</sub> and P(OR)<sub>2</sub>; or wherein Z and Z<sub>1</sub> together form the bridging group A-B-A<sub>1</sub>;

wherein each Z', Z'', Z<sub>1</sub>' and Z<sub>1</sub>'' is independently selected from the group consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR<sub>2</sub>,

5 COOR, halide, SiR<sub>3</sub>, P(O)R<sub>2</sub>, P(O)(OR)<sub>2</sub> and P(OR)<sub>2</sub>; or wherein Z' and Z together form the bridging group A'-B-A; Z' and Z together form a fused cycloaliphatic or aromatic group; Z<sub>1</sub> and Z<sub>1</sub>' together form the bridging group A<sub>1</sub>-B<sub>1</sub>-A<sub>1</sub>'; and/or Z<sub>1</sub> and Z<sub>1</sub>' together form a fused cycloaliphatic or aromatic group;

10 wherein each A, A', A<sub>1</sub> and A<sub>1</sub>' is independently selected from the group consisting of: O, CH<sub>2</sub>, NH, NR, S, CO and a bond;

wherein each B and B<sub>1</sub> is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12 carbon atoms, O, CH<sub>2</sub>, NH, NR, S, CO, SO<sub>2</sub>, P(O)R, P(O)OR, POR, SiR<sub>2</sub> and a bond;

15 wherein each T is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R'', YR', YR'', Y'R' and Y''R'; or wherein two T groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

20 wherein each T' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R'', YR', YR'', Y'R' and Y''R'; or wherein two T' groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

25 wherein each R, R' and R'' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, aralkyl and alkaryl of 1 to 22 carbon atoms; or wherein two R groups, two R' groups or two R'' group together form an alkylene or arelene group; and

30 wherein each Y, Y' and Y'' is independently selected from the group consisting of: O, CH<sub>2</sub>, NH, S and a bond between carbon and phosphorus; with the proviso that when the Y group at the 2' position is a bond between carbon and phosphorus, X' is hydrogen.

37. The process of claim 36, wherein said asymmetric reaction is selected from the group consisting of: hydrogenation, hydride transfer, allylic alkylation, hydrosilylation, hydroboration, hydrovinylation, hydroformylation, olefin metathesis, hydrocarboxylation, isomerization, cyclopropanation, Diels-Alder reaction, Heck reaction, isomerization, Aldol reaction, Michael addition, epoxidation, kinetic resolution and [m+n] cycloaddition wherein m = 3 to 6 and n = 2.

38. The process of claim 37, wherein said transition metal is selected from the group consisting of:

Ag, Pt, Pd, Rh, Ru, Ir, Cu, Ni, Mo, Ti, V, Re and Mn.

39. The process of claim 37, wherein said asymmetric reaction is hydrogenation and said substrate is selected from the group consisting of: imine, ketone, ethylenically unsaturated compound, enamine, enamide and vinyl ester.

40. The process of claim 37, wherein said asymmetric reaction is a silver-catalyzed asymmetric [3 +2] cycloaddition of an azomethine ylide with a dipolarophile.

41. The process of claim 37, wherein said asymmetric reaction is a palladium-catalyzed allylic alkylation and said substrate is an allylic ester.

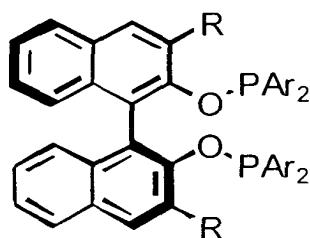
42. The process of claim 37, wherein said asymmetric palladium-catalyzed allylic alkylation reaction is a kinetic resolution reaction and said substrate is a racemic allylic ester.

43. The process of claim 37, wherein said asymmetric reaction is hydrogenation, said substrate is a beta-ketoester, said transition metal is Ru and said asymmetric compound is a beta-hydroxyester.

44. The process of claim 37, wherein said asymmetric reaction is hydrogenation, said substrate is an enamide, said transition metal is Ru and said asymmetric compound is a beta amino acid.

5 45. The process of claim 37, wherein said ligand is selected from the group consisting of compounds represented by the formula:

(a)

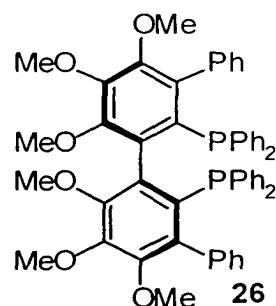


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wherein each R is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl and SiR<sub>3</sub>; and wherein each Ar is independently selected from the group consisting of: phenyl, substituted phenyl, aryl and substituted aryl;

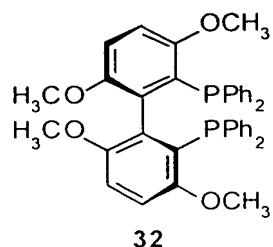
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(b)

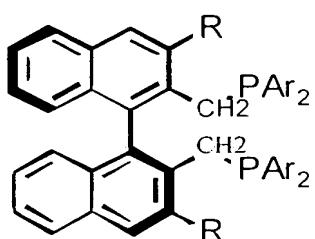


20

5 (c)



10 (d)



15 and a combination thereof.

46. The process of claim 45, wherein said asymmetric reaction is

hydrogenation, said substrate is a beta-ketoester, said transition metal is Ru and said asymmetric compound is a beta-hydroxyester.

47. The process of claim 45, wherein said asymmetric reaction is

hydrogenation, said substrate is an enamide, said transition metal is Ru and said asymmetric compound is a beta amino acid.

20